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DIALLYL DICARBONATE. A CONVENIENT REAGENT FOR THE SYNTHESIS OF ALLYL CARBAMATES.

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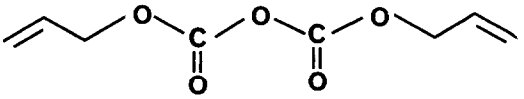
Abstract : *Diallyldicarbonate was prepared and used for the amino protection of various compounds including amino acids, amino sugars and nucleosides.*

The allyloxycarbonyl group was introduced by Stevens and Watanabe[1] for the protection of amino acids in 1950. Since then it has been seldomly used mainly because of the lack of convenient deprotection methods. However, in recent years, smooth deprotection methods have been devised which overcome this difficulty[2]. This has led to a new interest in this protecting group particularly in peptide[3] and nucleotide[4] synthesis. Furthermore, it has been recently demonstrated that alloc protection is a powerful tool in glycosidation reactions of aminosugars[5]. Although the allyloxycarbonyl group is readily introduced by means of the corresponding chloroformate, in some cases the latter reagent failed to give satisfactory results[4]. On the other hand, dicarbonates have become very popular to effect protection of amino groups. For instance $(BOC)_2O$ is now the most popular reagent for the synthesis of BOC-amino acids and dicarbonates have been recently extended to the preparation of Z-amino acids[6]. Moreover, the availability of dicarbonates has led to new trends in amino protection[7].

For these reasons, we wish to introduce the new diallyldicarbonate.



The reagent is easily obtained from the reaction of allyl chloroformate with sodium allyl carbonate in 82% yield (60% distilled yield)[8]. It is stable at room temperature and reacts readily with various amino compounds to yield the corresponding allyl carbamate (see Table). Except for the reaction with amino acids, the reagent does not require an additionnal base and the only by-products, carbon dioxide and allyl alcohol, are both volatile, which considerably simplifies the work-up of the reaction mixture. For instance, N-allyloxycarbonyl glucosamine was obtained analytically pure by simple evaporation of the reaction mixture. Although no reaction occured with adenosine in the conditions tested,the reagent was comparable to the more sophisticated

Table - Preparation of various allyloxycarbonylated amino compounds[a]

Entry	Substrate	Reagent	Reaction conditions	Yield %	b.p. °C/torr m.p. °C
1	$BuNH_2$	$(alloc)_2O$	CH_2Cl_2,1h,r.t.	93	118-119/15
2	Bz_2NH	"	"	92	194-195/0.07
3	$PhNH_2$	"	CH_2Cl_2,18h,r.t.	86	140-150/0.05
4	$Me_2N(CH_2)_3NH_2$	"	CH_2Cl_2,2h,r.t.	59	145-147/15
5	"	alloc-Cl	CH_2Cl_2/K_2CO_3,2h,r.t.	76	"
6	glucosamine	$(alloc)_2O$	H_2O/Dioxane,4h,r.t.	80	198-199
7	cytidine	"	H_2O/Dioxane,2h,reflux	67	212-214
8	"	alloc-OBt	"	55	212-214
9	adenosine	$(alloc)_2O$	H_2O/Dioxane,18h,reflux	0	
10	L-Gly	"	"	74	30-33
11	L-Phe	"	"	96	143[b]
12	L-Val	"	"	86	143[b]
13	L-Ala	"	"	88	138-140[b]
14	L-Met	"	"	96	118-120[b]
15	L-Ser	"	"	81	140-142[b]

a) New compounds gave correct spectroscopic and analytical data. b) DCHA salt

allyl 1-benzotriazolyl carbonate for the protection of cytidine. In one case, however, allyl chloroformate was superior to the dicarbonate. The reaction of $(alloc)_2O$ with N,N-dimethyl-1,3-diaminopropane led to the formation of the expected carbamate together with the symmetrical urea, whereas alloc-Cl through protection of the tertiary amine as its hydrochloride salt eliminates this side reaction. Finally, amino acids are easily protected as their allyl carbamates in good yield without formation of dipeptides.

We think that allyl dicarbonate, like other dicarbonates, conveniently supplements the known chloroformates as a reagent for the protection of amines.

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8- b.p. 65°C/0.05 Torr, i.r. (film) 1840, 1780, 1760 cm^{-1}, n.m.r. ($CDCl_3$), 4.7 ppm, 2H, doublet, 5.0-6.2 ppm, 3H, multiplet.

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